

Bioethanol production from marine algae biomass: prospect and troubles

Sản xuất ethanol từ sinh khối tảo: triển vọng và khó khăn

Review paper

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The increase of petroleum cost as well as global warming and climate change result in investigation to discover new renewable energy resources. Bioenergy is one of the most important sources that is concerning the scientists and industrial sector. Although bioethanol had to be known as one of the most important renewable energy sources in order to reduce greenhouse gases and global warming, there is a limited number of publications reporting on them. In this review, a brief overview is offered about bioethanol production from algae. It can be given a deeper insight in difficulties and promising potential of bioethanol from algae.

Sự gia tăng giá nhiên liệu hóa thạch cùng với cảnh báo toàn cầu về biến đổi khí hậu hướng đến việc nghiên cứu tìm ra những nguồn năng lượng có thể tái tạo. Năng lượng sinh học là một trong những nguồn quan trọng được các nhà khoa học và doanh nghiệp quan tâm. Mặc dù ethanol sinh học đã được biết đến như là một trong những dạng năng lượng tái tạo quan trọng nhất để giảm thiểu các khí nhà kính và cảnh báo toàn cầu, nhưng chỉ có một số ít bài báo về nó. Trong bài tổng quan này, chúng tôi giới thiệu vắn tắt việc sản xuất ethanol sinh học từ tảo. Nó đưa ra cái nhìn sâu hơn về những khó khăn và tiềm năng hứa hẹn của sản xuất ethanol sinh học từ tảo.

Keywords: biofuel, bioethanol, biomass, renewable energy, fossil fuel, algae

1. Introduction

In 2008, fossil fuels accounted for 88% of the global primary energy consumption (Brennan and Owende, 2010). However, the use of fossil fuels is now widely accepted as unsustainable due to depleting resources and the accumulation of greenhouse gases in the environment (Schenk et al., 2008). It has become increasingly important to develop abatement techniques and adopt policies to promote those renewable energy sources due to minimize the dependency on fossil reserves and also to maintain environmental and economic sustainability (Brennan and Owende, 2010; Prasad et al., 2007a,b; Singh et al., 2010a,b).

Biofuels are expected to reduce dependence on imported petroleum with associated political and economic vulnerability, reduce greenhouse gas emissions and other pollutants, and revitalize the economy by increasing demand and prices for agricultural products (Darici and Ocal, 2010; Tatli, 2009; Balat, 2010). Biofuels are an attractive alternative to current petroleum based fuels as they can be utilized as transportation fuels with little change to current technologies and have significant potential to improve

sustainability (Carere et al., 2008). There are two global liquid transportation biofuels: bioethanol and biodiesel, respectively (Demirbas, 2011). Bioethanol is good alternate fuel that is produced almost entirely from food crops (Hammond et al., 2008; Tan et al., 2009; Börjesson, 2009).

All automobile manufacturers produce vehicles that can readily use 10% ethanol or 85% ethanol (E85) blends for fuel, and ethanol can replace diesel in heavy vehicles as well. Nearly all fuel ethanol is produced by fermentation of corn glucose in the United States or sucrose in Brazil (Rosillo-Calle and Cortez, 1998). Generally, ethanol can be derived from any material that contains sugar. Today, raw materials used in the manufacture of ethanol by fermentation are classified as sugars, starches and cellulosic materials (Bailey and Ollis, 1986). Sugars can be converted to ethanol directly, while starches first have to be hydrolysed to fermentable sugars by the action of enzymes. Cellulose must likewise be converted to sugars before further fermentation, generally by the action of mineral acids (Bashir and Lee, 1994).

Research on improving bioethanol production has been accelerating for both ecological and economical reasons,

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primarily for its use as an alternative to petroleum based fuels (Prasad et al., 2007a). However, depleting water resources and utilization of arable land have put the feasibility of bioethanol under the scanner. The water footprint and land use for the production of biomass by cultivating various energy crops is given in Table 1. The extremely large arable land utilization for biomass production to be used as a raw material for production of bioeth-

anol as well as biofuels could result in shortages in basic foods, such as corn, cereals, soy, mustard, barley, etc. Thus, they have brought much controversy and debate on their sustainability (Goh and Lee, 2010). In this respect, cultivation of algae at sea water or industrial or other wastewater provides a possible solution for this energy issue.

Table 1. Water footprint, land use and bioethanol yield of various energy crops

	Water footprint (m ³ GJ ⁻¹)	Land use (m ² GJ ⁻¹)	Energy (GJ ha ⁻¹ a ⁻¹)	Biofuel yield (L ha ⁻¹ a ⁻¹)
Cassava	148	79	126	6,000
Wheat	93	305	33	1,560
Paddy rice	85	212	47	2,250
Corn grain	50	133	75	3,571
Potatoes	105	114	88	4,167
Sugar cane	50	81	124	5,882
Sugar beet	46	95	105	5,000
Sorghum	180	386	26	1,235
Soybean	383	386	26	1,235

Note: The above table was reviewed by Singh et al., 2011

Algae are considered as the only alternative to current bioethanol crops such as corn and soybean as they do not require arable land (Chisti, 2007; Hu et al., 2008; Singh et al., 2010c). The arable land could be used efficiently to grow food crops rather than biomass and oil seed crops for the production of biofuels. Water filled areas that are not suitable for growing food crops and industrial waste water can be used for the cultivation of algal biomass without any compromise with land and water resource for the production of bioethanol that will also not adversely affect the food cost (Singh et al., 2011). In addition, algae can be converted directly into energy, such as biodiesel, bioethanol and biomethanol and therefore can be a source of renewable energy.

2. Ethanol production from microalgae

Marine microalgae, or phytoplankton, are mostly represented in ocean populations: the best known are the diatoms (Bacillariophyta), the dinoflagellates (Dinophyta), the green algae (Chlorophyta) and the blue-green algae (Cyanophyta). The unicellular marine microalgae were considered to be an abounding resource for carotenoids, lipids, and polysaccharides, and were widely investigated in the fields of food supplements and bio-fuel production (Liau et al., 2010). While terrestrial plants in temperate climates can achieve a photoconversion efficiency of only below 1 %, microalgae can convert up to 5% of the solar energy into chemical energy (Rösch et al., 2012). Microalgae can be converted to biodiesel, bioethanol, bio-oil, biohydrogen and biomethane via thermochemical and biochemical methods (Demirbas, 2011). Using microalgae as a source of biofuels is not a new idea (Chisti, 1980), but it is now being taken seriously because of the increasing cost of petroleum and, more significantly, the

emerging concern about global warming arising from burning fossil fuels (Sawayama et al., 1995).

Certain species of microalgae have the ability of producing high levels of carbohydrates instead of lipids as reserve polymers. These species are ideal candidates for the production of bioethanol as carbohydrates from microalgae can be extracted to produce fermentable sugars. It has been estimated that approximately 5000–15,000 gal of ethanol/acre/year (46,760–140,290 L/ha) can be produced from microalgae. This yield is several orders of magnitude larger than yields obtained for other feedstocks (Table 2). Blue-green algae including *Spirogyra* species and *Chlorococum* sp. have been shown to accumulate high levels of polysaccharides both in their complex cell walls and as starch. This starch accumulation can be used in the production of bioethanol (Harun et al., 2010; Eshaq et al., 2011). Harun et al. have shown that the blue-green algae *Chlorococum* sp. produces 60% higher ethanol concentrations for samples that are pre-extracted for lipids versus those that remain as dried intact cells. This indicates that microalgae can be used for the production of both lipid-based biofuels and for ethanol biofuels from the same biomass as a means to increase their overall economic value (Jones and Mayfield, 2012).

The microalgae *Chlorella vulgaris*, particularly, has been considered as a promising feedstock for bioethanol production because it can accumulate up to 37% (dry weight) of starch. However, higher starch contents can also be obtained for optimized culture conditions (Hirano et al., 1997). *Chlorococum* sp. was also used as a substrate for bioethanol production under different fermentation conditions. Results showed a maximum bioethanol concentration of 3.83 g/L obtained from 10 g/L of lipid-extracted microalgae debris (Harun et al., 2009).

Table 2. Ethanol yield from different sources

Source	Ethanol yield (gal/acre)	Ethanol yield (L/ha)
Corn stover	112–150	1,050–1,400
Wheat	277	2,590
Cassava	354	3,310
Sweet sorghum	326–435	3,050–4,070
Corn	370–430	3,460–4,020
Sugar beet	536–714	5,010–6,680
Switch grass	1,150	10,760
Microalgae	5,000–15,000	46,760–140,290

Note: The above table was reviewed by Mussatto et al., 2010

Bioethanol production from microalgae begins with the collection and drying of algae that have been cultivated in a suitable for water environment. In the next step of the process, the algae mass is ground and hydrolyzed and then the hydrolyzed mass is fermented and finally distilled (Demirbas and Demirbas, 2010). Production of ethanol by using microalgal as raw material can be performed according to the following procedure. In the first step, the starch of microalgae is released from the cells with the aid of mechanical equipment or an enzyme. When the cells begin to degrade, *Saccharomyces cerevisiae* yeast is added to the biomass to begin fermentation. The product of fermentation is ethanol. The ethanol is drained from the tank and pumped to a holding tank to be fed to a distillation unit. Ethanol was produced with microalgal photosynthesis and intracellular anaerobic fermentation (Hirano et al., 1997; Pimentel, 2003; Pimentel and Patzek, 2005; Demirbas, 2011). One hectare algae farm on wasteland can produce over 10–100 times of oil as compared to any other known source of oil-crops. While a crop cycle may take from three months to three years for production, algae can start producing oil within 3–5 days and thereafter oil can be harvested on daily basis.

3. Ethanol production from macroalgae

Seaweeds are classified into three groups: green, brown, and red, and they contain various types of glucans which are polysaccharides composed of glucose, though the concentration of these glucans is known to be relatively low. Seaweed was proposed as one of the most promising biomass materials that can be easily converted to ethanol, since seaweeds are known to contain a low concentration of lignin or no lignin at all. Three types of seaweed including sea lettuce, chigaiso, and agar weed were used as representatives of green, brown, and red seaweeds, respectively, and methods for obtaining high concentrations of ethanol (bioethanol) from these seaweeds were investigated (Yanagisawa et al., 2011). An ethanol yield of more than 3% was obtained from these seaweeds.

Today, the most important microorganisms applied for ethanol production are the yeast *Saccharomyces cerevisiae* and the bacterium *Zymomonas mobilis*. However, both these ethanol producers have a very narrow substrate range. Horn et al. have reported that *Zymobacter palmae*

could produce ethanol from mannitol in seaweed extract, if some supply of oxygen was provided. In addition, the possibility of ethanol production from *Laminaria hyperborea* extracts was evaluated, focusing on the yeast *Pichia angophorae* and its potential of utilising both mannitol and laminaran as substrates. Initial experiments with seaweed extract showed that *Pichia angophorae* was able to utilise both mannitol and laminaran for ethanol production (Horn, 2000b). Ethanol can be produced from the mannitol and laminaran contained in extracts from *L. hyperborea* fronds. *Z. palmae* was able to produce ethanol from mannitol, while *P. angophorae* could utilise both carbohydrates for ethanol production.

Bioethanol from algae holds significant potential due to their low percentage of lignin and hemicellulose as compared to other lignocellulosic plants (Harun et al., 2010). While having low lignin content, macroalgae contain significant amount of sugars (at least 50%) that could be used in fermentation for bioethanol production (Wi et al., 2009). However, in certain marine algae such as red algae the carbohydrate content is influenced by the presence of agar, a polymer of galactose and galactopyranose. Current research seeks to develop methods of saccharification to unlock galactose from the agar and further release glucose from cellulose leading to higher ethanol yields during fermentation (Wi et al., 2009; Yoon et al., 2010).

4. Trends and challenges of bioethanol production from algae

Ethanol production worldwide has strongly increased since the oil crises in 1970. Its market grew from less than a billion liters in 1975 to more than 39 billion liters in 2006, and is expected to reach 100 billion liters in 2015 (Licht, 2006). The international ethanol market has been stimulated by governmental politics of incentive to the use of renewable fuels. Although in expansion, the international market is very regional, with the largest producers being also the largest consumers (Mussatto et al., 2010). Brazil was the main exporter (3.5 gal), and the United States, Japan and the Europe were the main importers. In Brazil, the ethanol use as bio-fuel is very common. In the 80s, more than half of the Brazilian cars used 95% anhydrous ethanol, however, the lack of sugar and its high prices decreased this value in the subsequent years (Solomon et al., 2007). Nowadays, almost all the Brazilian vehicles use ethanol, in the pure form or in

mixture with the gasoline, where ethanol corresponds up to 25% of the mixture. In the United States, ethanol is actually used in two forms: mixed with gasoline in the maximum proportion of 10%, or in mixtures containing 85% ethanol and 15% gasoline, as an alternative fuel (EIA, 2006). In a next step, the supply of ethanol mixtures with gasoline will be expanded to the whole country and some efforts will be also directed to increase the ethanol percentage in the mixture to 10% (Prasad et al., 2007b).

Although bioethanol used as renewable fuel is one of the positive trends for sustainable development, there are some difficulties in production and consumption. Ethanol is an intermediate in the complete digestion of organic material and is produced by specific microbial strains. An obvious practical problem with ethanol production is that the microbial culture may have to be protected against contamination of other microbes. Thus, ethanol production should take place under controlled conditions to prevent contamination problems (Horn et al., 2000a,b).

The complex composition of seaweeds makes it a difficult substrate to ferment to ethanol by one or a few strains of microbes. There are a number of limited researchs done on ethanol production from seaweeds. The reason may be the complex composition of seaweeds, containing several different carbohydrates. Finding a microorganism that can ferment all the different carbohydrates to ethanol is not very likely. Besides, alginate, as a major component in brown algae, may not be fermented to ethanol since the redox balance in the glycolytic oxidation of uronic acids to pyruvate is maintained. Moreover, utilisation of seaweed carbohydrates for ethanol production is probably only of economic interest when integrated with a balanced and total utilisation of the seaweed material. Energy production from seaweeds will only be economic if the harvesting costs are low. Conversion of biomass from marine algae into ethanol could be economically feasible since some algae hydrolysates can contain more total carbohydrate and hexose sugars than some terrestrial, lignocellulosic biomass feedstock (Horn, 2000).

4. Conclusions

Bioethanol production from marine algae has great potential for sustainable development. Several algae species have been studied for, such as *Spirogyra* species, *Chlorococum* sp., *Chlorella vulgaris*, and *Laminaria hyperborean*. However, there have been difficulties in order to widely commercialize bioethanol as an alternative to petroleum based fuels, and it needs more studies in the future to dissolve these troubles.

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